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ION SUPPRESSION FOR STUDYING ETCH INHIBITOR LAYERS(U)
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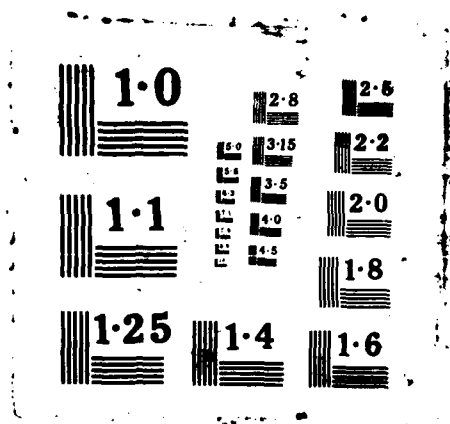
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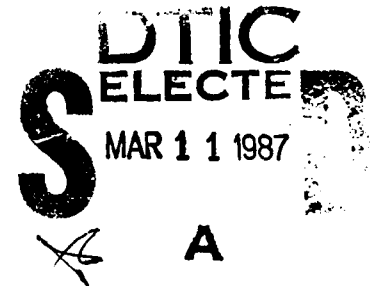
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Ion Suppression for Studying Etch Inhibitor Layers

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Abstract

Etch inhibitor layers are key to anisotropy for a number of dry etch processes, yet little is known about these layers because of the difficulty in analyzing them on the side walls where they form. In this paper we will show that a Al grid suspended above an etching surface can be used to suppress ion bombardment on the etch surface and allow the inhibitor to form on large horizontal surfaces which can easily be analyzed. This method was used to look at the polymeric inhibitor formed during Si etching in SF_6/C_2F_5 with and without the presence of photoresist.

Introduction

Dry etch processes rely on a combination of chemical and ion driven etching to achieve directional or anisotropic profiles. At low pressures (10 mT) where the ratio of the ion flux to reactive neutral flux is high, ion assisted etching dominates and anisotropic profiles are readily achievable. However, there is considerable interest in operating at higher pressures above 100 mT where higher etch rates can be achieved because of the higher concentration of reactive neutrals in the gas phase. This is especially true for single wafer etchers which need high etch rates to reach acceptable through-put rates. Unfortunately, the reactive neutrals at higher concentrations often react

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spontaneously with the material to be etched resulting in isotropic profiles. To suppress this chemical etching in the lateral direction and to maintain high etch rates in the vertical direction sidewall etch inhibitor layers are often used.

Despite the widespread use of sidewall layers for anisotropic etching of poly-Si(1), silicides and aluminum(2), little is known about their properties because of the difficulty of analyzing a thin film on the edge of a step only a micron high. As shown in Fig. 1, qualitatively it is understood that these layers form on the vertical sidewall where there is little ion bombardment, and that their formation is prevented or limited on the horizontal surfaces where ion bombardment is a maximum. In most cases these layers are believed to be composed of halocarbon polymers because their effect on lateral etching is only seen when there is a high carbon to halogen ratio in the source gas, and increases in the carbon to halogen ratio leads to polymer formation on all surfaces. Coburn(3) has suggested that for the case of silicon etching in a mixed halocarbon gas that a thin film of fluoropolymer (a few monolayers thick) could retard the etch rate by lowering the reaction probability of the etching species. Inorganic sidewall layers may also be important in that anisotropic etching of silicon has been reported(4) in gas mixtures of SF_6/O_2 at 150 mT with no carbon sources present.

In this paper we will report on the use of a localized ion suppression grid to study the effect of ion bombardment on sidewall layer formation and etch rate. The goal with local ion suppression is to reduce the ion flux to a horizontal surface without effecting the neutral radical flux, and thus to simulate the sidewall conditions in a horizontal area which is large enough to be easily analyzed by available surface analysis tools. To test the effectiveness of this method, we will focus on the etching of silicon using a mixture of SF_6 and C_2ClF_5 with and without the presence of resist. X-ray photoelectron spectroscopy (XPS) will be used to analyze the etched surfaces for the different conditions and these results will be correlated with etch rate results.

Ion Suppression

In a glow discharge, sheath regions form between the bulk glow, or plasma, region and all surfaces, in order to reflect the highly mobile electrons back into the plasma. The electric fields in the sheath form this barrier to electrons flowing out of the plasma. These fields accelerate the positive ions coming out of the plasma, and are thus responsible for the energetic ion bombardment of the wafer surface. This acceleration process is in competition with ion-neutral collisions. Ordinarily the sheath thickness is \leq than the ion mean free path length (λ_m) between collisions, and so most of the ions make it across the sheath without any collisions and thus receive the maximum energy from the sheath. If a metal grid at the same potential as the wafer is placed above the wafer at a distance L, as shown in Fig. 2, the sheath field will terminate at the grid, and the space between the grid and the wafer will be field free. Ions which

make it through the grid will now face an increased probability of energy loss by collision, and there will be no field to help them regain this energy. Since the probability of collision goes as $1 - e^{-L/\lambda_m}$, the mean ion energy will rapidly decrease as L is made larger than λ_m . Thus a grid held above a wafer can be used to substantially suppress ion bombardment.

The criteria for choosing a grid for suppressing ion bombardment is that it be non-reactive with the etch chemistry, that it be fine enough to indeed terminate the sheath field, and that it be open enough not to significantly reduce the reactive neutral flux onto the wafer. For fluorine based chemistries bare aluminum which has been plasma conditioned in a fluorine plasma is a good choice for the grid material, while for chlorine based chemistries an oxide coated aluminum grid might be best. The grid opening should be near equal to the expected sheath thickness to terminate the sheath field and yet not restrict the neutrals.

Silicon Etching in $\text{SF}_6/\text{C}_2\text{ClF}_5$

The experiment to be reported in this paper is based on previous work (5) on silicon etching by this group which will be summarized in this section. The etching of silicon in a 50:50 mixture of $\text{SF}_6/\text{C}_2\text{ClF}_5$ is on the threshold of apparent sidewall inhibitor formation in that the etch profile is nearly isotropic when a oxide mask is used and is nearly anisotropic when a resist mask is used. This effect is shown in Fig. 3 for two wafers etched at the same time in a batch etcher. It was also reported that the range of the apparent polymer precursors was about 2.7 cm as shown in Fig. 4. This figure shows an experiment in which one edge of a oxide patterned wafer was coated with resist before etching again in the same $\text{SF}_6/\text{C}_2\text{ClF}_5$ mixture for 15 min. The results were that the etch depth was uniform across the wafer, while the undercut rapidly increased as the distance from the resist was increased until the undercut saturated at value equal to the etch depth at a distance of 2.7 cm from the resist.

A explanation of this etch process is that the SF_6 is supplying free F which is responsible the chemical etching of the silicon. The C_2ClF_5 is supplying some polymer precursors in the form of CF and CF_2 , but their concentration is too low to form a sufficient sidewall layer to block the F etching. When the resist is introduced, the erosion of the resist by the ion bombardment and by the free fluorine acts as an additional source of CF and CF_2 , and now the sidewall layer is sufficient to block the lateral etching.

This etch process is of interest for evaluating the usefulness of the present grid technique because it offers the opportunity of locally controlling the polymer precursor concentration at the same time the ion bombardment is locally controlled by the use of a grid. In this way most of the internal plasma etch parameters can be held near constant, by etching samples at the same time

with different ion bombardment fluxes and different polymer precursor concentrations. A key assumption for evaluating the experimental results will be that the free fluorine concentration was the same for all the samples. This assumption depends on the grid and the resist not significantly affecting the fluorine concentration. In the case of the resist the uniform etch depth for the two wafers shown in fig. 2 and across the wafer in fig. 3, indicates that the resist had little effect on the free F concentration over the wafers.

Experiment

The silicon samples were etched at the same time in a batch etcher with and without a grid, and with and without the presence of photoresist nearby. Figure 5 shows the experimental configuration used. As shown, an 0.8 mm thick aluminum plate was placed over each of the silicon wafers to set the separation of the grid from the wafer surface. The plates had a number of 6mm square holes to allow etching of the wafer in these regions. Over two of the holes on each plate, an aluminum screen (0.25mm wire on 1.4mm centers) was placed to form the ion suppression grid. Both of the Al electrode and the grid/plate assemblies were ground. One of the grid/plate assemblies was coated with photoresist on its top surface while the other plate was left bare.

The etch conditions were: plasma mode, a gas flow of 150 sccm each of SF_6 and C_2ClF_6 , a pressure of 150 mT, a etch time of 20 minutes, a RF power of 0.4 watts/cm^2 at 13.56 Mhz, and a electrode spacing of 3 cm. Assuming a mean collision cross-section of $6.1 \times 10^{-15} \text{ cm}^2$, the ion mean free path in the collision space should be 0.33 mm. Allowing for the thickness of the screen, L should be 1.2 mm or 3.6 mean free paths. The wafers were 3" <100> p-type silicon with a resistivity of between 10 and 20 ohm-cm. The resist was Shipley 1470 and was baked at 120°C for 60 minutes after applying with a brush. Using the etch conditions above both assemblies were conditioned in a discharge for 45 minutes before inserting the wafers under the plates in order to reduce fluorine recombination on their surfaces.

After etching, the wafers were broken to prepare XPS samples, and a Dektak IIA was used to measure the etch depths as shown in Table 1. The presence of the grid and the resist decreased the etch depth by 14 and 29%, respectively. The combined grid/resist case had the greatest impact on etch depth with a 93% reduction in etch depth from the open/no resist case.

XPS Measurements

Using a Mg K_α x-ray source, the etched surfaces were characterized by x-ray photospectroscopy (XPS) measurements in a UHV system. Initial results were disappointing in that the results were not repeatable and did not correlate with the etch conditions. The problem was found to be related to the air exposure of the samples between the time they were etched and were loaded into the UHV system. Figure 6 shows the full XPS spectra for three exposure times (24 hrs, 2

hrs and 20 min) for open/resist samples. It is seen that the etched surfaces are affected by air exposure with the F peak totally disappearing and the O peak increasing for long air exposures. This is a limitation which strongly recommends in-situ surface analysis. However, since the samples with short air exposures (10 to 20 minutes) give distinct XPS spectra which correlated with etch conditions and which are repeatable for separate runs, the results are useful for shedding light on the properties of these inhibitor layers.

In order to determine the thickness range of the expected surface layers, the surfaces were XPS sputtered profiled by alternating XPS measurements with 1 minute of argon sputtering until the surface layer was removed. The argon beam had a sputter rate of 8 Å/min. Figure 7 shows the uncorrected peak area for the major peaks versus sputter time for grid/resist and open/resist samples which had been exposed to air for 2 hrs. Focusing on the grid/resist results, we see that the F, C, and Cl peaks monotonically decrease as the surface is eroded. In contrast the O and the SiO₂ peaks initially increase and then fall off. These results indicate a fluorocarbon layer at the top surface with a SiO₂ rich layer at the silicon surface and a total thickness in the range of 30 Å. These results are similar to those of Oehrlein et al (6) who studied fluorocarbon layer formation on silicon surfaces exposed to the ion bombardment during RIE oxide etching in CF₄/H₂. They found 50 Å layers also with oxide rich layers at the silicon interface. In both their and our case this oxide is attributable to the air exposure. Now focusing on the open/resist case shown in Fig. 7, we see that the surface layer is somewhat thinner in that the Si peak saturated after only 1 minute, or 8 Å, of sputtering. Since the layer thicknesses are near the escape depth of the silicon photoelectrons for this measurement, the Si peak area should be a measure of the layer thickness, provided the silicon concentration in the layer is low.

Table 2 shows the XPS peak areas and the concentration percentages from full spectra scans for the samples shown in Table 1. The air exposure was kept to a minimum (10 to 20 minutes) for these measurements. The data shown has been cross section corrected. The Si (2p) peak decreases as one goes down the table in the direction of decreasing etch rate. This suggests an increasing surface layer thickness as part of the cause for the decreasing etch depth. The total C(1s) peak does not show any significant changes. The O(1s) peak shows the same trend as the Si peak, and is consistent with a O rich region at the Si interface as discussed previously. The F(1s) peak shows the greatest change with etch condition in that it increases by 12X as the corresponding etch depth decreases by 14 x. Clearly fluorine is a major component in the inhibitor layer. The Cl(2p) peak tends to follow the F peak, but its concentration is at the noise level of this measurement.

Focusing on the carbon 1s peak, Fig. 8 shows higher resolution scans for this peak. We see that there is significant structure in this peak which can be

deconvolved into separate peaks using a Gaussian peak-fitting algorithm. It is well known that there is a chemical shift in the binding energy of C to higher energies as the bonding of carbon is changed from graphitic or C-H bonding to carbon-fluorine bonding. Oehrlein et al(7) has reported the binding energies for C-C, C-C-F, C-F, and C-2F bonding as 284.6, 286.9, 289.2, and 291.2 eV, respectively. Clearly, Figure 8 shows that the carbon bonding on the etched surface shifts from mainly graphitic to fluorine dominated as the etch depth decreases. Table 3 shows these results in tabular form. Our peak positions agree within 0.5 eV to those reported by Oehrlein. In addition, we found a peak at 287.9 eV which Rice et al (8) assigned to C-Cl bonding.

Discussion

The etch depth results in Table 1 clearly show that the grid had the desired effect of allowing an inhibitor layer to form for the grid/resist case since there was a dramatic decrease in etch depth for this case. The XPS results show that there is a thin carbon layer, or residue, on all of the etched silicon surfaces with the carbon bonding being affected by both the ion bombardment and the presence of resist nearby. The ion bombardment appears to cause the dehalogenation of the polymeric residue, leading to the increased graphitic character as can be seen in Fig. 8 where the C-C peak at 285 eV increases for the open cases over the grid cases. The polymer precursors from the resist erosion appear to be in competition with the ion bombardment in that they tend to halogenate the residue as seen with the increase in the C-2F peak at 291.7 eV when resist is nearby. The etch inhibitor property of this residue appears to be associated with the degree of halogenation of this layer. This can be seen in Table 4 where the average etch rate for the different cases are listed in comparison to the various measures for the degree of halogenation. Included are: a) the total surface concentration (in atom percent) for fluorine, b) the atom percent of F-C-F groups, c) the overall F to C ratio, and d) the F to C ratio in the residue. The last is given by:

$$F_C/C = (\text{Area of C-F Peak} + 2 \times \text{Area of the C-2F Peak}) / \text{Total Area of the C(1s) Spectral Envelope}.$$

In comparing the two C/F ratios, we find that much of the F in the residue layer is not bonded to C. It is likely that much of this excess F is bonded to Si and that one explanation for the inhibitor properties of these layers is that they block the desorption of the etch by-products SiF_2 and SiF_4 . As for the thickness of these residue layers, the XPS sputter profile results yield a thickness of $\approx 30 \text{ \AA}$ for the grid/resist case and $\approx 10 \text{ \AA}$ for the open/resist case. These thicknesses are confirmed with the decrease in the Si peak as we go down Table 2 in the direction of decreasing etch rate. Since the XPS probe only has a depth sensitivity of $\approx 40 \text{ \AA}$, the decreasing Si peak implies increasing layer thickness with a maximum thickness $< 40 \text{ \AA}$. This indicates that the residue thickness plays an important role in etch blocking.

In conclusion, we have shown that a metal grid can be used to suppress ion bombardment during plasma etching and that this can be used to study inhibitor layer formation by allowing these layers to form in areas large enough to be easily accessible by surface analysis tools. In applying such grids to study inhibitor layer formation during the etching of silicon in $\text{SF}_6/\text{C}_2\text{ClF}_5$, it was found that the etch blocking layer is $\approx 30\text{\AA}$ and that it is a highly halogenated carbon layer. In regions exposed to the full ion bombardment the carbon layer thickness decreases and is less halogenated.

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Table 1 Shows localized etch conditions and the resulting silicon etch depth after a single etch run for 20 min etch in $\text{SF}_6/\text{C}_2\text{F}_5$.

Condition	Depth (μm)	Normalized Depth
Open/No Resist	5.90	1.00
Open/Resist	5.10	0.86
Grid/No Resist	4.15	0.70
Grid/Resist	0.42	0.07

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Table 2 XPS peak areas (*) and total surface concentration in atom percent for the localized etch conditions shown. Corrected for cross section.

		Si(2p)	C(2s)	Cl(2p)	O(1s)	F(1s)
Open/No Res.	*	157828	17270	----	13763	4533
	%	81.61	8.93	----	7.12	2.34
Open/Resist	*	169581	18147	2199	13836	22019
	%	75.11	8.04	0.97	6.13	9.75
Grid/No Res.	*	188371	19280	2201	13836	35598
	%	72.65	7.43	0.85	5.34	13.73
Grid/Resist	*	152395	22611	5661	10496	71639
	%	57.99	8.60	2.15	3.99	27.26

Table 3 XPS carbon 1s peak positions and percent of total carbon surface concentration for the localized etch conditions shown.

	C-C C-H	C-C-F _n	C-Cl	C-F	C-F ₂
Position ΔeV	285.0 ±0.2	286.7 ±0.6	287.9 ±0.3	289.3 ±0.3	291.7 ±0.3
Open/No Res.	75.1	11.9	----	10.2	2.9
Open/Resist	59.9	9.0	----	15.4	15.7
Grid/No Res.	38.0	19.4	2.7	17.4	22.5
Grid/Resist	16.3	6.7	4.2	31.8	41.0

Table 4 Average etch rate calculated from table 1, the total surface concentration (in atom percent) for fluorine, the atom percent of C-2F groups, the overall F to C ratio, and the F to C ratio in the residue.

Etch Rate $\text{\AA}/\text{min}$	$\%F_T$	$\%C_{C-2F}$	F_T/C_T Ratio	F_C/C Ratio
2950	2.34	0.22	0.26	0.16
2548	9.75	1.26	1.20	0.47
2090	13.73	1.67	1.85	0.63
212	27.26	3.53	3.13	1.14

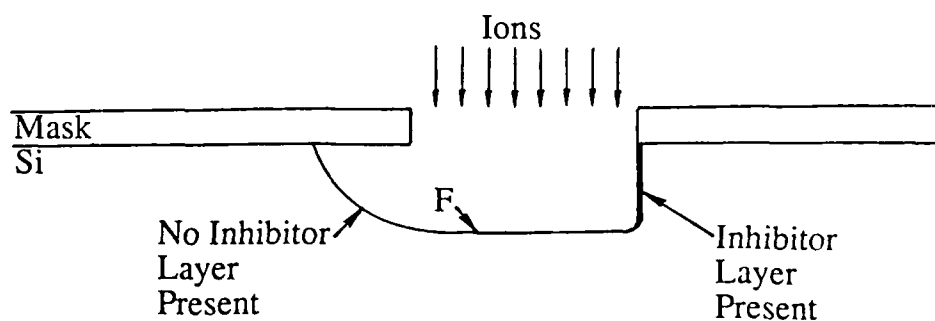


Figure 1. Cross section showing sidewall inhibitor layer blocking lateral etching.

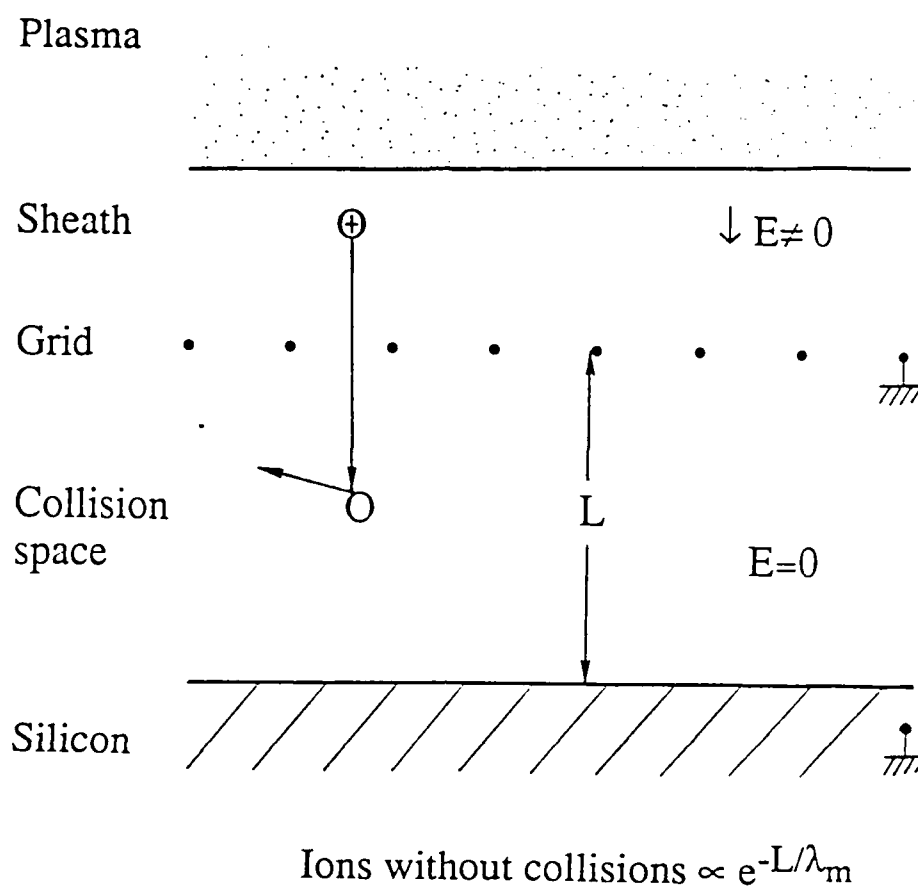
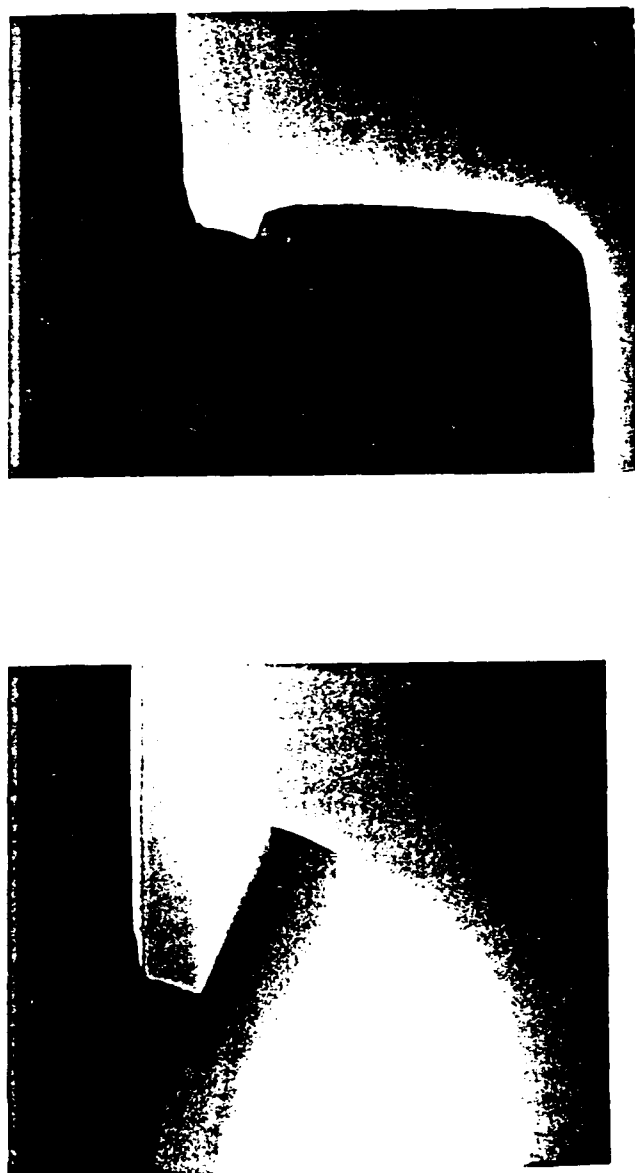


Figure 2. Sheath region showing ion collision space created by grid.



—3 μ m—

Figure 3. SEM cross sections of silicon wafer showing effect of a) oxide mask and b) oxide/resist mask on etch profile. Etch conditions: 50:50 $\text{SF}_6/\text{C}_2\text{ClF}_5$, 0.36 W/cm², 150 mT and plasma mode.

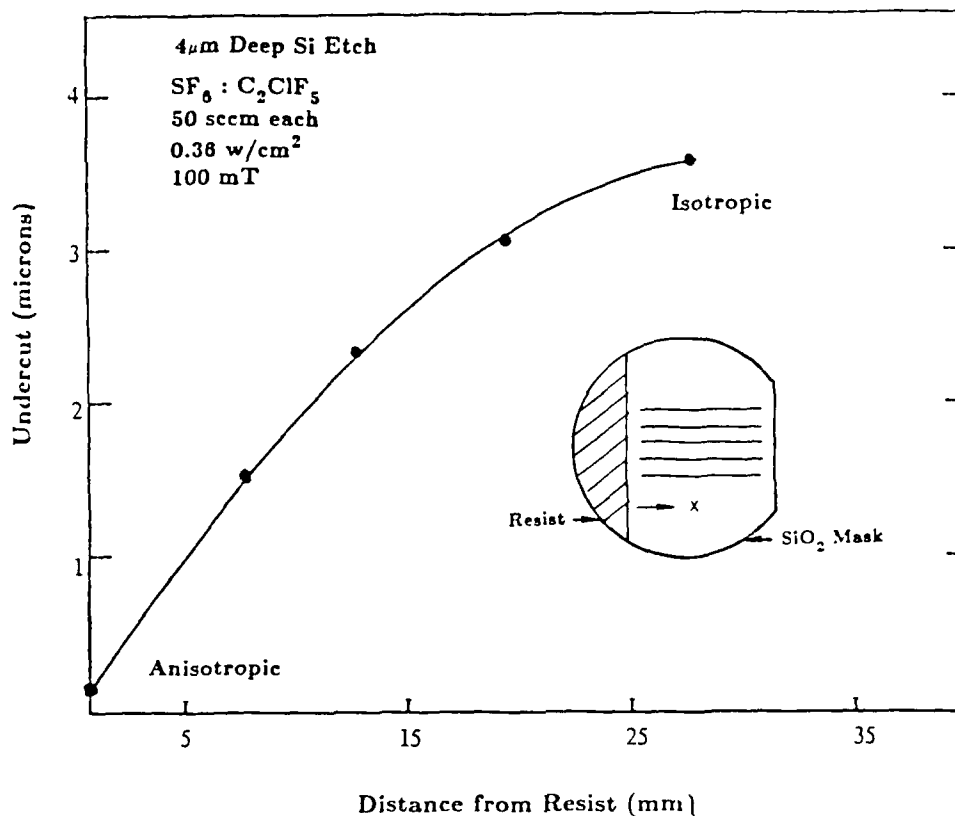


Figure 4. Experiment showing effect of resist on undercut as a function of distance from resist.

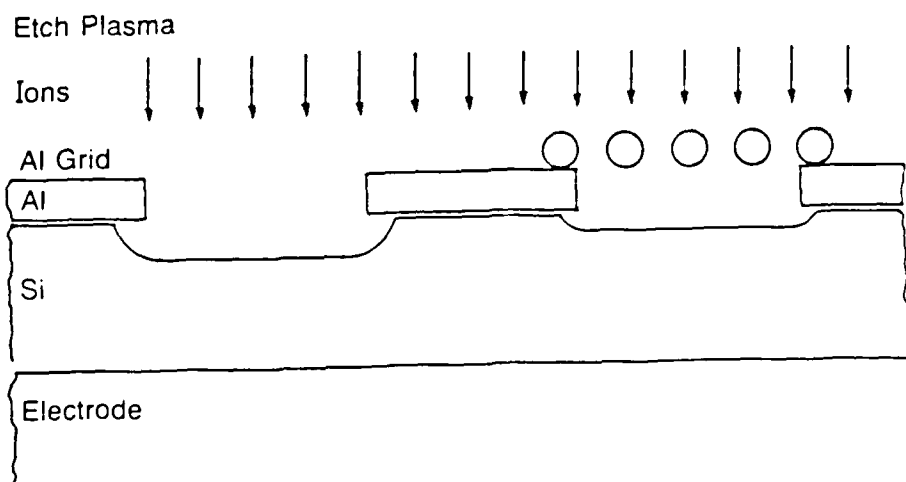
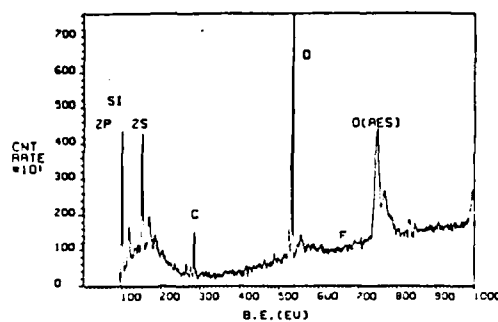
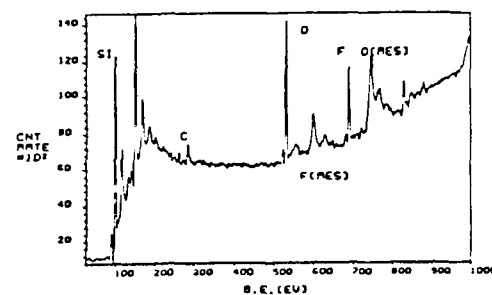


Figure 5. Plate/Grid assembly used for localized ion suppression. Resist, when used, on top side of Al plate.

24 hrs



2 hrs



20 min

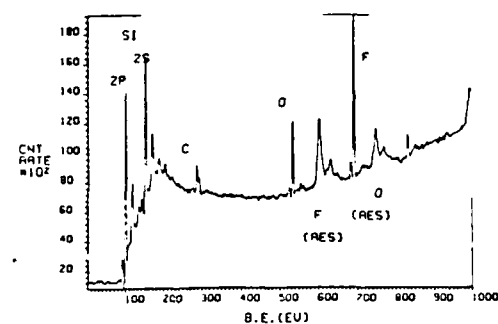


Figure 6. XPS full scan after a) 24 hrs, b) 2 hrs and c) 20 min air exposure of etched surfaces.

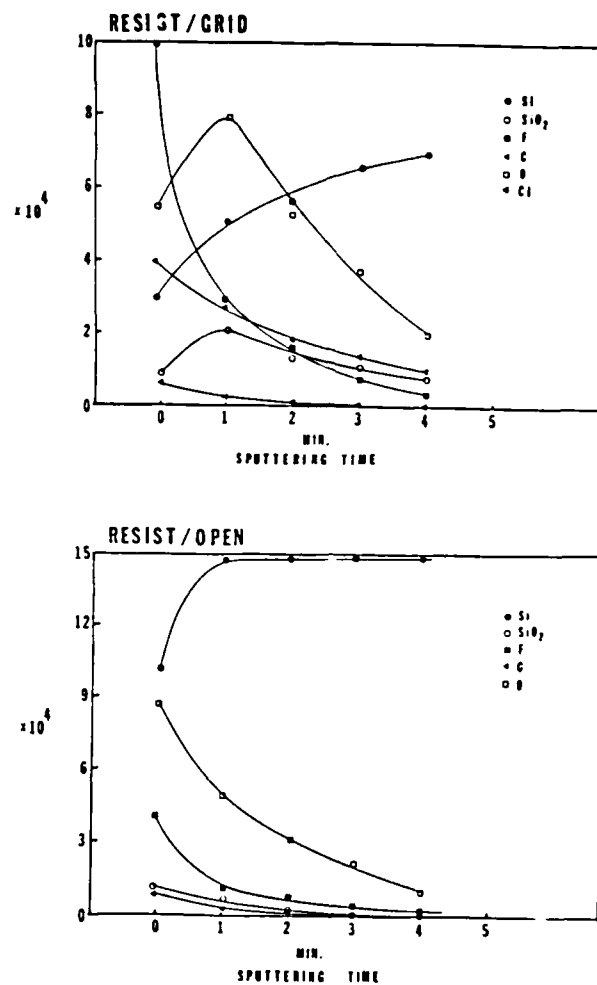


Figure 7. XPS sputter profiles of a) resist/grid and b) resist/open samples after 2 hrs air exposure. Sputter rate $\approx 8 \text{ \AA/min}$.

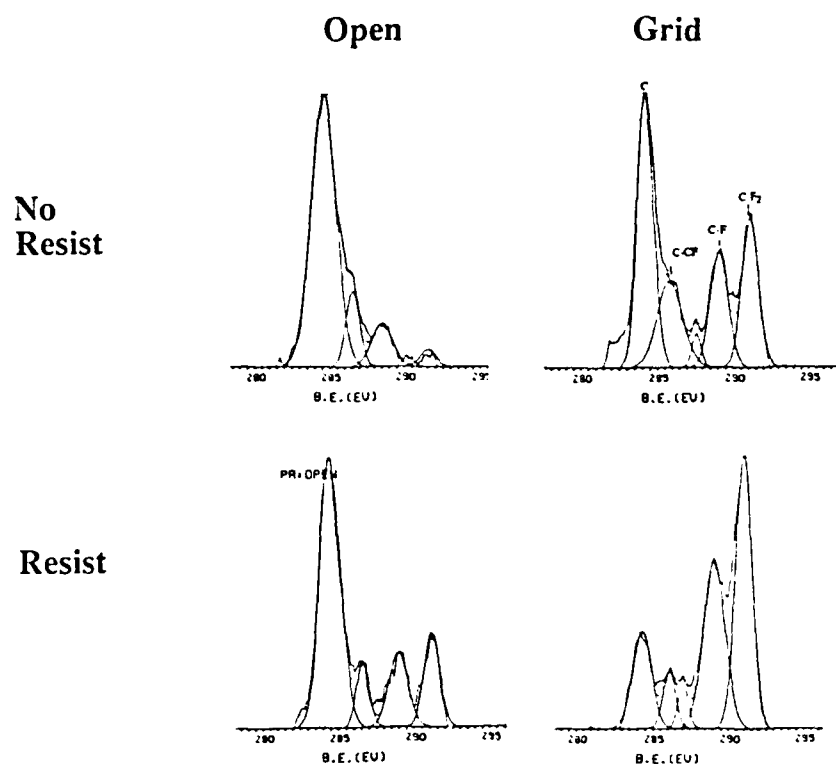


Figure 8. XPS scan of carbon 1s peaks for a) Open/No Resist, b) Grid/No Resist, c) Open/Resist and b) Grid/Resist samples.

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